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(54) METHOD FOR DESULFURIZATION OF LIQUID OIL CONTAINING ORGANIC SULFUR COMPOUND

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for desulfurization of a liquid oil containing organic sulfur compounds, with which sulfur in the liquid oil can be efficiently removed to ≤ 1 ppm sulfur content, and a first adsorbent (first desulfurizing agent) and a second desulfurizing agent have a long life, and a method for producing hydrogen for a fuel cell from the desulfurized liquid oil by a partial oxidation reforming treatment, an autothermal reforming treatment or a steam reforming treatment.

SOLUTION: This method for desulfurization of a liquid oil containing an organic sulfur compound comprises treating the liquid oil containing the organic sulfur compound with an oxidizing agent, bringing the treated liquid oil into contact with the first and then the second desulfurizing agents. This method for producing hydrogen for a fuel cell comprises desulfurizing the liquid oil containing the organic sulfur compound and bringing the desulfurized liquid oil into contact with a partial reforming catalyst, an autothermal reforming catalyst or a steam reforming catalyst.

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CLAIMS

[Claim(s)]

[Claim 1] The desulfurization approach of the organosulfur compound content liquefied oil characterized by making the adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further after processing an organosulfur compound content liquefied oil with an oxidizer.

[Claim 2] The desulfurization approach of an organosulfur compound content liquefied oil according to claim 1 which is a kind at least that an organosulfur compound content liquefied oil is chosen from natural gas, alcohol, the ether, LPG, naphtha, a gasoline, kerosene, gas oil, a fuel oil, an asphaltene oil, an oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL, a waste plastic oil, and biotechnology fuel.

[Claim 3] An oxidizer Oxygen, air, a nitrogen tetroxide, ozone, chlorine, a bromine, sodium metaperiodate, A potassium dichromate, potassium permanganate, a chromic anhydride, a hypochlorous acid, The mixture of the mixture of a fault hydrogen chloride, a peracetic acid, and a hydrogen peroxide and an acetic acid, performic acid, and a hydrogen peroxide and formic acid, The mixture of a meta-chloro perbenzoic acid, a fault chloroacetic acid, and a hydrogen peroxide and a chloroacetic acid, The mixture of fault dichloroacetic acid, and a hydrogen peroxide and dichloroacetic acid, a fault trichloroacetic acid, The mixture of the mixture of a hydrogen peroxide and a trichloroacetic acid, fault trifluoroacetic acid, and a hydrogen peroxide and trifluoroacetic acid, The desulfurization approach of the organosulfur compound content liquefied oil according to claim 1 or 2 which is chosen from the mixture of the mixture of a fault meta-sulfonic acid, a hydrogen peroxide, a meta-sulfonic acid, a fault salicylic acid and a hydrogen peroxide, and a salicylic acid, persulfuric acid, and a hydrogen peroxide and a sulfuric acid and which is a kind at least.

[Claim 4] The desulfurization approach of an organosulfur compound content liquefied oil according to claim 1 to 3 which is a kind at least that an adsorbent is chosen from a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, activated carbon, and insoluble synthetic resin.

[Claim 5] The desulfurization approach of an organosulfur compound content liquefied oil according to claim 1 to 4 that the 2nd devulcanizing agent is the thing which is chosen from nickel, silver, chromium, manganese, iron, cobalt, copper, zinc, palladium, iridium, platinum, a ruthenium, a rhodium, and gold and which contains a kind at least.

[Claim 6] The desulfurization approach of the organosulfur compound content liquefied oil according to claim 1 to 5 which is what uses an adsorbent in a -40-100-degree C temperature requirement, and uses the 2nd devulcanizing agent in a -40-300-degree C temperature requirement.

[Claim 7] The manufacture approach of the hydrogen for fuel cells characterized by making a partial oxidation reforming catalyst, an autothermal reforming catalyst, or a steam-reforming catalyst contact after desulfurizing an organosulfur compound content liquefied oil using an approach according to claim 1 to 6.

[Claim 8] The manufacture approach of the hydrogen for fuel cells according to claim 7 that a partial oxidation reforming catalyst, an autothermal reforming catalyst, or a steam-reforming

catalyst is a ruthenium system catalyst or a nickel system catalyst.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About the desulfurization approach of an organosulfur compound content liquefied oil, and the manufacture approach of the hydrogen for fuel cells, can remove efficiently the sulfur content in an organosulfur compound content liquefied oil to 1 ppm or less, and the life of a devulcanizing agent processing [partial oxidation refining], processes [autothermal-refining-] or processes [steam-reforming-] in more detail, the desulfurization approach of a long organosulfur compound content liquefied oil, and an organosulfur compound content [by which desulfurization processing was carried out by the approach] liquefied oil, and this invention relates to the approach of manufacturing the hydrogen for fuel cells.

[0002]

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed to electrical energy, it has the features that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles.

[0003] According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. Research of an activity of petroleum system hydrocarbon oils, such as naphtha of a petroleum system, a gasoline, and kerosene, is made by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel (GTL) which uses natural gas as a raw material, biotechnology fuel, the waste plastic oil, and the pan.

[0004] When using a fuel cell for a noncommercial use or automobiles, since the distribution system is fixed, a gas station, a dealer, etc. are advantageous [the above-mentioned petroleum system hydrocarbon oil] as sources of hydrogen the top where storage and handling are easy. However, a petroleum system hydrocarbon oil has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. Moreover, sulfur content may also mix liquefied oils, such as GTL, biotechnology fuel, such as vegetable oil methyl ester, and a waste plastic oil, during transport or storage. When manufacturing hydrogen using such an organosulfur compound content liquefied oil, generally steam reforming and the approach of partial-oxidation-refining-processing or autothermal refining processing are used for the bottom of existence of a reforming catalyst in this fuel oil. In such refining processing, since poisoning of the above-mentioned reforming catalyst is carried out by the sulfur content in fuel oil, it usually needs to carry out desulfurization processing of the sulfur content in fuel oil from the point of a catalyst life at 1 ppm or less.

[0005] By the way, as the desulfurization approach of a petroleum fraction, a sulfur compound is oxidized with an oxide and the approach of carrying out separation clearance using lifting of the melting point or the boiling point is learned (JP,4-72387,A). Moreover, in order to promote the reaction of a sulfur compound and an oxidizer, how to introduce an oxidation catalyst is also

learned (JP,11-140462,A). However, when applying these approaches to desulfurization of an organosulfur compound content liquefied oil, since a minute amount [organosulfur compound], sufficient separation recovery is not obtained, and it has not resulted in practical level.

[0006]

[Problem(s) to be Solved by the Invention] This invention aims at offering partial-oxidation refining, autothermal refining, or the method of carrying out steam-reforming processing and manufacturing the hydrogen for fuel cells for the organosulfur compound content liquefied oil which can remove efficiently the sulfur content in an organosulfur compound content liquefied oil to 1 ppm or less and by which it was made under the above-mentioned situation, and desulfurization processing also of the life of an adsorbent (the 1st devulcanizing agent) and the 2nd devulcanizing agent was carried out by the long desulfurization approach of an organosulfur compound content liquefied oil, and this desulfurization approach.

[0007]

[Means for Solving the Problem] this invention person found out that the object of this invention could be effectively attained by making the adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further after processing an organosulfur compound content liquefied oil with an oxidizer, as a result of repeating research wholeheartedly. This invention is completed based on this knowledge.

[0008] That is, the summary of this invention is as follows.

1. Desulfurization approach of organosulfur compound content liquefied oil characterized by making adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further after processing organosulfur compound content liquefied oil with oxidizer.
2. Desulfurization approach of organosulfur compound content liquefied oil of said one publication which is kind at least that organosulfur compound content liquefied oil is chosen from natural gas, alcohol, the ether, LPG, naphtha, gasoline, kerosene, gas oil, fuel oil, asphaltene oil, oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL, waste plastic oil, and biotechnology fuel.

Oxidizer 3. Oxygen, Air, Nitrogen Tetroxide, Ozone, Chlorine, Bromine, Sodium Metaperiodate, A potassium dichromate, potassium permanganate, a chromic anhydride, a hypochlorous acid, The mixture of the mixture of a fault hydrogen chloride, a peracetic acid, and a hydrogen peroxide and an acetic acid, performic acid, and a hydrogen peroxide and formic acid, The mixture of a meta-chloro perbenzoic acid, a fault chloroacetic acid, and a hydrogen peroxide and a chloroacetic acid, The mixture of fault dichloroacetic acid, and a hydrogen peroxide and dichloroacetic acid, a fault trichloroacetic acid, The mixture of the mixture of a hydrogen peroxide and a trichloroacetic acid, fault trifluoroacetic acid, and a hydrogen peroxide and trifluoroacetic acid, Said 1 which is chosen from the mixture of the mixture of a fault meta-sulfonic acid, a hydrogen peroxide, a meta-sulfonic acid, a fault salicylic acid and a hydrogen peroxide, and a salicylic acid, persulfuric acid, and a hydrogen peroxide and a sulfuric acid and which is a kind at least, or the desulfurization approach of an organosulfur compound content liquefied oil given in 2.

4. Desulfurization approach of organosulfur compound content liquefied oil given in either [as which an adsorbent is chosen from a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, activated carbon, and insoluble synthetic resin / which is a kind at least / said] 1-3.

5. Desulfurization approach of organosulfur compound content liquefied oil given in either [whose 2nd devulcanizing agent is the thing which is chosen from nickel, silver, chromium, manganese, iron, cobalt, copper, zinc, palladium, iridium, platinum a ruthenium, a rhodium, and gold, and which contains a kind at least / said] 1-4.

6. Desulfurization approach of organosulfur compound content liquefied oil given in either [which is what uses an adsorbent in a -40-100-degree C temperature requirement, and uses the 2nd devulcanizing agent in a -40-300-degree C temperature requirement / said] 1-5.

7. Manufacture approach of hydrogen for fuel cells characterized by making partial oxidation reforming catalyst, autothermal reforming catalyst, or steam-reforming catalyst contact after desulfurizing organosulfur compound content liquefied oil using approach of publication to either

[said] 1-6.

8. Manufacture approach of hydrogen for fuel cells said seven publications that partial oxidation reforming catalyst, autothermal reforming catalyst, or steam-reforming catalyst is ruthenium system catalyst or nickel system catalyst.

[0009]

[Embodiment of the Invention] Below, this invention is explained at a detail. After the desulfurization approach of the organosulfur compound content liquefied oil (it may be hereafter called stock oil) of this invention processes stock oil with an oxidizer, it is characterized by making the adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further.

[0010] Although it will not be limited as an oxidizing agent in this invention especially if it oxidizes to a sulfoxide or a sulfone, thiophenes specifically For example, oxygen, air, a nitrogen tetroxide, ozone, chlorine, a bromine, sodium metaperiodate, A potassium dichromate, potassium permanganate, a chromic anhydride, a hypochlorous acid, The mixture of the mixture of a fault hydrogen chloride, a peracetic acid, and a hydrogen peroxide and an acetic acid, performic acid, and a hydrogen peroxide and formic acid, The mixture of a meta-chloro perbenzoic acid, a fault chloroacetic acid, and a hydrogen peroxide and a chloroacetic acid, The mixture of fault dichloroacetic acid, and a hydrogen peroxide and dichloroacetic acid, a fault trichloroacetic acid, The mixture of the mixture of a hydrogen peroxide and a trichloroacetic acid, fault trifluoroacetic acid, and a hydrogen peroxide and trifluoroacetic acid, The mixture of the mixture of a fault meta-sulfonic acid, a hydrogen peroxide, a meta-sulfonic acid, a fault salicylic acid and a hydrogen peroxide, and a salicylic acid, persulfuric acid, and a hydrogen peroxide and a sulfuric acid etc. can be mentioned. Although it can be used even if these oxidizers are independent, it can also be used combining two or more sorts.

[0011] Although the processing conditions by the oxidizer change with oxidizers, generally the range of temperature is 0-100 degrees C, and a pressure is the range of ordinary pressure - 1 MPa-G. Subsequently, although stock oil is contacted to the adsorbent as the 1st devulcanizing agent, a silica, an alumina, a silica alumina, a zelite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, activated carbon, insoluble synthetic resin, etc. can be mentioned as an adsorbent. Although it can be used even if these adsorbents are independent, it can also be used combining two or more sorts. About the configuration of an adsorbent, the shape of the shape of powder, the letter of grinding, a pellet type, and a tablet and a bead can be mentioned suitably.

[0012] The approach of filling up an adsorption tower with an adsorbent and circulating this stock oil may be used for the contact to the stock oil and the adsorbent which were oxidized, and standing or the approach of stirring may be used for it in the stock oil oxidized by containers, such as a tank which fixed the adsorbent to the interior. The range of temperature of -40-100 degrees C is [the conditions in that case] desirable. - If there is a possibility that the fluidity of stock oil may fall if lower than 40 degrees C and it is higher than 100 degrees C, the adsorption capacity of an adsorbent falls and is not desirable. It is the range of -20-80 degrees C still more preferably. Moreover, as for a pressure, it is desirable that it is the range of ordinary pressure - 1 MPa-G.

[0013] Then, although stock oil is contacted to the 2nd devulcanizing agent, adsorption desulfurization of stock oil can be efficiently performed by using the 2nd devulcanizing agent. That is, it becomes extensible [temperature reduction of adsorption desulfurization of the 2nd devulcanizing agent or break time]. As this 2nd devulcanizing agent, there is especially no limit and it may use the adsorption devulcanizing agents or hydrodesulfurization catalysts other than the 1st devulcanizing agent. Especially a limit has that desirable from which there is nothing, the thing which is chosen from nickel, silver, chromium, manganese, iron, cobalt, copper, zinc, palladium, iridium, platinum, a ruthenium, a rhodium, and gold, and which contains a kind at least could be mentioned, and those metals were supported by porosity support especially as the adsorption devulcanizing agent. The aforementioned adsorbent can be mentioned as the porosity support. That with which the metal which contains nickel or silver at least especially was supported by porosity support is desirable. By carrying out hydrogen reduction beforehand, these

adsorption devulcanizing agents can raise the desulfurization engine performance. Moreover, when using a hydrodesulfurization catalyst as the 2nd devulcanizing agent, little addition of the hydrogen may be carried out. In addition, the temperature which uses the 2nd devulcanizing agent has desirable -40–300 degrees C. – If there is a possibility that the fluidity of stock oil may fall and it is higher than 300 degrees C when lower than 40 degrees C, the adsorption capacity of an adsorbent falls and is not desirable. It is the range of -20–250 degrees C still more preferably. Moreover, as for a pressure, it is desirable that it is the range of ordinary pressure – 1 MPa–G. [0014] The method of contacting directly the stock oil desulfurized by the 1st devulcanizing agent to the 2nd devulcanizing agent as the desulfurization approach by the 2nd devulcanizing agent is desirable. Moreover, stock oil is desulfurized by the 1st devulcanizing agent in somewhere else, and the 2nd devulcanizing agent may be made to contact, just before carrying out a refining reaction. In the approach of this invention, as an organosulfur compound content liquefied oil, there is especially no limit and it can mention suitably natural gas, alcohol, the ether, LPG, naphtha, a gasoline, kerosene, gas oil, a fuel oil, an asphaltene oil, an oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL, a waste plastic oil, biotechnology fuel, etc. Kerosene is desirable especially and it is desirable that a sulfur content content especially applies to JIS No. 1 kerosene 80 ppm or less also in kerosene. This JIS No. 1 kerosene is obtained by desulfurizing the rough kerosene obtained by carrying out atmospheric distillation of the crude oil. If this kerosene remains as it is, it does not need to turn into JIS No. 1 kerosene, but it needs to reduce sulfur content. It is desirable to carry out desulfurization processing by the hydrotreating process currently generally enforced industrially as an approach of reducing this sulfur content.

[0015] The manufacture approach of the hydrogen for fuel cells which is the second invention of this application is an approach of manufacturing hydrogen, by doing in this way and contacting the stock oil which carried out desulfurization processing with a partial oxidation reforming catalyst, an autothermal reforming catalyst, or a steam-reforming catalyst (all being summarized and it only being hereafter, called a reforming catalyst). As a reforming catalyst used in the approach of this invention, there is especially no limit, out of the well-known thing known as a reforming catalyst of a hydrocarbon from the former, can choose the thing of arbitration suitably and can use it. As such a reforming catalyst, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. A kind is sufficient as the above-mentioned support metal, and it may combine two or more sorts. In these catalysts, the thing (henceforth a nickel system catalyst) which made nickel support, and the thing (henceforth a ruthenium system catalyst) which made the ruthenium support are desirable, and the effectiveness which controls the carbon deposit in partial oxidation refining, autothermal refining, or steam reforming is large.

[0016] In the case of this nickel system catalyst, the amount of support of nickel has the desirable range of 3 – 60 mass % on support criteria. Under by 3 mass %, there is a possibility that the activity of partial oxidation refining, autothermal refining, or steam reforming may not fully be demonstrated, on the other hand, the improvement effectiveness of catalytic activity of having balanced that amount of support will seldom be accepted, but this amount of support will become disadvantageous economically rather, if 60 mass % is exceeded. When catalytic activity, profitability, etc. are taken into consideration, the more desirable amount of support of this nickel is five to 50 mass %, and its range of 10 – 30 mass % is especially desirable.

[0017] Moreover, in the case of a ruthenium system catalyst, the amount of support of a ruthenium has the desirable range of 0.05 – 20 mass % on support criteria. Under by 0.05 mass %, there is a possibility that the activity of partial oxidation refining, autothermal refining, or steam reforming may not fully be demonstrated, on the other hand, the improvement effectiveness of catalytic activity of having balanced that amount of support will seldom be accepted, but this amount of support will become disadvantageous economically rather, if 20 mass % is exceeded. When catalytic activity, profitability, etc. are taken into consideration, the more desirable amount of support of this ruthenium is 0.05 to 15 mass %, and its range of 0.1 – 2 mass % is especially desirable.

[0018] As a reaction condition in partial oxidation refining processing, as for 400–1,100 degrees

C, and oxygen (O₂)/carbon (mole ratio), 0.2 to 0.8 is adopted, and for ordinary pressure - 5MPa and temperature, the conditions of 0.1-100hr-1 are usually adopted for a pressure, as for liquid hourly space velocity (LHSV). moreover — as the reaction condition in autothermal refining processing — usually — a pressure — as for 0.1-1, and liquid hourly space velocity (LHSV), the conditions of 1,000-100,000hr-1 are adopted [ordinary pressure - 5MPa and temperature / 400-1,100 degrees C, and steam/carbon (mole ratio)] for 0.1-10, and oxygen (O₂)/carbon (mole ratio), as for 0.1-2hr-1 and the rate (GHSV) between gas space-time.

[0019] furthermore, a ratio with the carbon which originates in a steam and fuel oil as a reaction condition in steam-reforming processing — steam/carbon (mole ratio) — usually — 1.5-10 — desirable — 1.5-5 — it is more preferably selected in 2-4. If there is a possibility that the amount of generation of hydrogen may fall [steam/carbon (mole ratio)] less than by 1.5 and 10 is exceeded, a superfluous steam is needed and a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0020] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of fuel oil may be promoted, carbon may deposit in a catalyst or a reaction tube wall via the generated radical, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650-800 degrees C is desirable. If there is fear which is not enough and it exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable.

[0021] reaction pressure — usually — ordinary pressure - 3 MPa-G — desirable — the range of ordinary pressure - 1 Ma-G — it is — moreover, LHSV — usually — 0.1-100hr-1 — it is the range of 0.2-50hr-1 preferably. In order that CO obtained by the above-mentioned partial oxidation refining, autothermal refining, or steam reforming may have an adverse effect on hydrogen generation in the manufacture approach of the above-mentioned hydrogen, it is CO₂ by the reaction about this. It is desirable to carry out and to remove CO. Thus, the hydrogen for fuel cells can be manufactured efficiently.

[0022]

[Example] Next, although an example explains this invention concretely, it is not restricted to these examples at all. The JIS No. 1 kerosene to be used is shown in the 1st table.

[0023]

[A table 1]

第1表

| 燃料油 | JIS1号灯油 |
|-----------|---------|
| 硫黄分 (ppm) | 48 |
| 蒸留性状 (°C) | |
| 初留温度 | 153 |
| 10%留出温度 | 176 |
| 30%留出温度 | 194 |
| 50%留出温度 | 209 |
| 70%留出温度 | 224 |
| 90%留出温度 | 249 |
| 终点 | 267 |

[0024] <Preparation of oxidation-treatment stock oil> oxidation kerosene 1 (oxidizer: meta-chloro perbenzoic acid)

5g (purity: about 70%) was added for the meta-chloro perbenzoic acid to 16l. of JIS No. 1 kerosene, it stirred at the room temperature for 8 hours, and oxidation kerosene 1 was obtained. Oxidation kerosene 2 (oxidizing agent: hydrogen-peroxide + salicylic acid) 13.6g was added for 4.5g (30% hydrogen peroxide) of hydrogen peroxide solution, and a salicylic

acid to 16l. of JIS No. 1 kerosene, it stirred at the room temperature for 8 hours, and oxidation kerosene 2 was obtained.

[0025] [Example 1] 2l. of oxidation kerosene 1 was held in the container with a capacity of 5l., [Wakogel(trademark) C-200 and Wako Pure Chem industrial company make] made from silica gel 200g was added as an adsorbent, and it stirred at the room temperature for 24 hours. Then, filtration separated kerosene and an adsorbent. Subsequently, 15ml weighing capacity of the nickel support diatomaceous earth (nickel50 mass %, the whole nickel support diatomaceous earth criteria, nickel-5249, Engelhard Corp. make) was carried out as the 2nd devulcanizing agent, and the coil made from stainless steel with a bore of 17mm was filled up. After carrying out temperature up to 120 degrees C the bottom of ordinary pressure, and among the hydrogen air current and holding for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and nickel support diatomaceous earth was activated. Then, reaction temperature was lowered and held at 150 degrees C. To the coil, the collected aforementioned kerosene was circulated by liquid-space-velocity 10hr-1. The sulfur concentration of the kerosene after 5-hour progress was 0.13 ppm.

[0026] [Example 2] In the example 1, it carried out similarly except having used oxidation kerosene 2 instead of oxidation kerosene 1. The sulfur concentration of the kerosene after 5-hour progress was 0.15 ppm.

[Example 3] 2l. of oxidation kerosene 1 was held in the container with a capacity of 5l., [Wakogel (trademark) C-200 and Wako Pure Chem industrial company make] made from silica gel 200g was added as an adsorbent, and it stirred at the room temperature for 24 hours. Then, filtration separated kerosene and an adsorbent. Subsequently, 15ml weighing capacity of the silver support silica alumina (the whole Ag5 mass %;Ag support silica-alumina criteria, N-633L, the JGC chemistry company make) was carried out as the 2nd devulcanizing agent, and the coil made from stainless steel with a bore of 17mm was filled up. After carrying out temperature up to 170 degrees C the bottom of ordinary pressure, and among the nitrogen air current and holding for 3 hours, the temperature was lowered to the temperature fall. To the coil, the collected aforementioned kerosene was circulated by liquid-space-velocity 10hr-1. The sulfur concentration of the kerosene after 5-hour progress was 0.15 ppm.

[0027] [Example 1 of a comparison] 2l. of oxidation kerosene 2 was held in the container with a capacity of 5l., [Wakogel(trademark) C-200 and Wako Pure Chem industrial company make] made from silica gel 200g was added as an adsorbent, and it stirred at the room temperature for 24 hours. Then, filtration separated kerosene and an adsorbent. The sulfur concentration of the kerosene was 6.9 ppm.

[0028] [Example 2 of a comparison] In the example 1, it carried out similarly except having used the JIS No. 1 kerosene which was not oxidized instead of oxidation kerosene 1. The sulfur concentration of the kerosene after 5-hour progress was 12 ppm.

[0029] [Example 4] (steam-reforming processing)

Steam-reforming processing was carried out with the refining vessel with which the lower stream of a river of the 2nd devulcanizing agent of an example 1 was filled up with 20ml (amount of ruthenium support 0.5 mass %, support criteria) of ruthenium system reforming catalysts. Refining processing conditions are a pressure:atmospheric pressure, the steam/carbon 2.5 (mole ratio), LHSV:1.0hr-1, inlet temperature:500 degree C, and outlet temperature:750 degree C. Consequently, the invert ratio in the refining outlet of 200 hours after was 100%. Moreover, the sulfur content of the desulfurization processing kerosene in this reaction period was 0.2 ppm or less.

[0030]

[Effect of the Invention] According to the desulfurization approach of the organosulfur compound content liquefied oil of this invention, adsorption treatment of the sulfur content in an organosulfur compound content liquefied oil can be efficiently carried out to 1 ppm or less, and the life of an adsorbent (the 1st devulcanizing agent) and the 2nd devulcanizing agent is also long. Moreover, the hydrogen for fuel cells can be effectively manufactured for the organosulfur compound content liquefied oil by which desulfurization processing was carried out by this desulfurization approach partial oxidation refining, autothermal refining, or by carrying out steam

reforming.

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TECHNICAL FIELD

[Field of the Invention] About the desulfurization approach of an organosulfur compound content liquefied oil, and the manufacture approach of the hydrogen for fuel cells, can remove efficiently the sulfur content in an organosulfur compound content liquefied oil to 1 ppm or less, and the life of a devulcanizing agent processing [partial oxidation refining], processes [autothermal-refining-] or processes [steam-reforming-] in more detail, the desulfurization approach of a long organosulfur compound content liquefied oil, and an organosulfur compound content [by which desulfurization processing was carried out by the approach] liquefied oil, and this invention relates to the approach of manufacturing the hydrogen for fuel cells.

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PRIOR ART

[Description of the Prior Art] In recent years, the new energy technique is in the limelight from the environmental problem, and the fuel cell attracts attention as one of the new energy technique of this. When this fuel cell makes hydrogen and oxygen react electrochemically, chemical energy is transformed to electrical energy, it has the features that the utilization effectiveness of energy is high, and utilization research is positively made as a noncommercial use, industrial use, or an object for automobiles.

[0003] According to the class of electrolyte used for this fuel cell, the type of a phosphoric-acid mold, a melting carbonate mold, a solid acid ghost mold, a solid-state macromolecule mold, etc. is known. Research of an activity of petroleum system hydrocarbon oils, such as naphtha of a petroleum system, a gasoline, and kerosene, is made by the town gas which, on the other hand, uses as a principal component the liquefied natural gas which makes a methanol and methane a subject, and this natural gas as a source of hydrogen, the synthetic liquid fuel (GTL) which uses natural gas as a raw material, biotechnology fuel, the waste plastic oil, and the pan.

[0004] When using a fuel cell for a noncommercial use or automobiles, since the distribution system is fixed, a gas station, a dealer, etc. are advantageous [the above-mentioned petroleum system hydrocarbon oil] as sources of hydrogen the top where storage and handling are easy. However, a petroleum system hydrocarbon oil has the problem that there are many contents of sulfur content, compared with the thing of a methanol or a natural gas system. Moreover, sulfur content may also mix liquefied oils, such as GTL, biotechnology fuel, such as vegetable oil methyl ester, and a waste plastic oil, during transport or storage. When manufacturing hydrogen using such an organosulfur compound content liquefied oil, generally steam reforming and the approach of partial-oxidation-refining-processing or autothermal refining processing are used for the bottom of existence of a reforming catalyst in this fuel oil. In such refining processing, since poisoning of the above-mentioned reforming catalyst is carried out by the sulfur content in fuel oil, it usually needs to carry out desulfurization processing of the sulfur content in fuel oil from the point of a catalyst life at 1 ppm or less.

[0005] By the way, as the desulfurization approach of a petroleum fraction, a sulfur compound is oxidized with an oxide and the approach of carrying out separation clearance using lifting of the melting point or the boiling point is learned (JP,4-72387,A). Moreover, in order to promote the reaction of a sulfur compound and an oxidizer, how to introduce an oxidation catalyst is also learned (JP,11-140462,A). However, when applying these approaches to desulfurization of an organosulfur compound content liquefied oil, since a minute amount [organosulfur compound], sufficient separation recovery is not obtained, and it has not resulted in practical level.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the desulfurization approach of the organosulfur compound content liquefied oil of this invention, adsorption treatment of the sulfur content in an organosulfur compound content liquefied oil can be efficiently carried out to 1 ppm or less, and the life of an adsorbent (the 1st devulcanizing agent) and the 2nd devulcanizing agent is also long. Moreover, the hydrogen for fuel cells can be effectively manufactured for the organosulfur compound content liquefied oil by which desulfurization processing was carried out by this desulfurization approach partial oxidation refining, autothermal refining, or by carrying out steam reforming.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention aims at offering partial-oxidation refining, autothermal refining, or the method of carrying out steam-reforming processing and manufacturing the hydrogen for fuel cells for the organosulfur compound content liquefied oil which can remove efficiently the sulfur content in an organosulfur compound content liquefied oil to 1 ppm or less and by which it was made under the above-mentioned situation, and desulfurization processing also of the life of an adsorbent (the 1st devulcanizing agent) and the 2nd devulcanizing agent was carried out by the long desulfurization approach of an organosulfur compound content liquefied oil, and this desulfurization approach.

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MEANS

[Means for Solving the Problem] this invention person found out that the object of this invention could be effectively attained by making the adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further after processing an organosulfur compound content liquefied oil with an oxidizer, as a result of repeating research wholeheartedly. This invention is completed based on this knowledge.

[0008] That is, the summary of this invention is as follows.

1. Desulfurization approach of organosulfur compound content liquefied oil characterized by making adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further after processing organosulfur compound content liquefied oil with oxidizer.
2. Desulfurization approach of organosulfur compound content liquefied oil of said one publication which is kind at least that organosulfur compound content liquefied oil is chosen from natural gas, alcohol, the ether, LPG, naphtha, gasoline, kerosene, gas oil, fuel oil, asphaltene oil, oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL, waste plastic oil, and biotechnology fuel.
- Oxidizer 3. Oxygen, Air, Nitrogen Tetroxide, Ozone, Chlorine, Bromine, Sodium Metaperiodate, A potassium dichromate, potassium permanganate, a chromic anhydride, a hypochlorous acid, The mixture of the mixture of a fault hydrogen chloride, a peracetic acid, and a hydrogen peroxide and an acetic acid, performic acid, and a hydrogen peroxide and formic acid, The mixture of a meta-chloro perbenzoic acid, a fault chloroacetic acid, and a hydrogen peroxide and a chloroacetic acid, The mixture of fault dichloroacetic acid, and a hydrogen peroxide and dichloroacetic acid, a fault trichloroacetic acid, The mixture of the mixture of a hydrogen peroxide and a trichloroacetic acid, fault trifluoroacetic acid, and a hydrogen peroxide and trifluoroacetic acid, Said 1 which is chosen from the mixture of the mixture of a fault meta-sulfonic acid, a hydrogen peroxide, a meta-sulfonic acid, a fault salicylic acid and a hydrogen peroxide, and a salicylic acid, persulfuric acid, and a hydrogen peroxide and a sulfuric acid and which is a kind at least, or the desulfurization approach of an organosulfur compound content liquefied oil given in 2.
4. Desulfurization approach of organosulfur compound content liquefied oil given in either [as which an adsorbent is chosen from a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, activated carbon, and insoluble synthetic resin / which is a kind at least / said] 1-3.
5. Desulfurization approach of organosulfur compound content liquefied oil given in either [whose 2nd devulcanizing agent is the thing which is chosen from nickel, silver, chromium, manganese, iron, cobalt, copper, zinc, palladium, iridium, platinum a ruthenium, a rhodium, and gold, and which contains a kind at least / said] 1-4.
6. Desulfurization approach of organosulfur compound content liquefied oil given in either [which is what uses an adsorbent in a -40-100-degree C temperature requirement, and uses the 2nd devulcanizing agent in a -40-300-degree C temperature requirement / said] 1-5.
7. Manufacture approach of hydrogen for fuel cells characterized by making partial oxidation reforming catalyst, autothermal reforming catalyst, or steam-reforming catalyst contact after desulfurizing organosulfur compound content liquefied oil using approach of publication to either

[said] 1-6.

8. Manufacture approach of hydrogen for fuel cells said seven publications that partial oxidation reforming catalyst, autothermal reforming catalyst, or steam-reforming catalyst is ruthenium system catalyst or nickel system catalyst.

[0009]

[Embodiment of the Invention] Below, this invention is explained at a detail. After the desulfurization approach of the organosulfur compound content liquefied oil (it may be hereafter called stock oil) of this invention processes stock oil with an oxidizer, it is characterized by making the adsorbent as the 1st devulcanizing agent contact, and making the 2nd devulcanizing agent contact further.

[0010] Although it will not be limited as an oxidizing agent in this invention especially if it oxidizes to a sulfoxide or a sulfone, thiophenes specifically For example, oxygen, air, a nitrogen tetroxide, ozone, chlorine, a bromine, sodium metaperiodate, A potassium dichromate, potassium permanganate, a chromic anhydride, a hypochlorous acid, The mixture of the mixture of a fault hydrogen chloride, a peracetic acid, and a hydrogen peroxide and an acetic acid, performic acid, and a hydrogen peroxide and formic acid, The mixture of a meta-chloro perbenzoic acid, a fault chloroacetic acid, and a hydrogen peroxide and a chloroacetic acid, The mixture of fault dichloroacetic acid, and a hydrogen peroxide and dichloroacetic acid, a fault trichloroacetic acid, The mixture of the mixture of a hydrogen peroxide and a trichloroacetic acid, fault trifluoroacetic acid, and a hydrogen peroxide and trifluoroacetic acid, The mixture of the mixture of a fault meta-sulfonic acid, a hydrogen peroxide, a meta-sulfonic acid, a fault salicylic acid and a hydrogen peroxide, and a salicylic acid, persulfuric acid, and a hydrogen peroxide and a sulfuric acid etc. can be mentioned. Although it can be used even if these oxidizers are independent, it can also be used combining two or more sorts.

[0011] Although the processing conditions by the oxidizer change with oxidizers, generally the range of temperature is 0-100 degrees C, and a pressure is the range of ordinary pressure - 1 MPa-G. Subsequently, although stock oil is contacted to the adsorbent as the 1st devulcanizing agent, a silica, an alumina, a silica alumina, a zeolite, a titania, a zirconia, a magnesia, a zinc oxide, clay, clay, diatomaceous earth, activated carbon, insoluble synthetic resin, etc. can be mentioned as an adsorbent. Although it can be used even if these adsorbents are independent, it can also be used combining two or more sorts. About the configuration of an adsorbent, the shape of the shape of powder, the letter of grinding, a pellet type, and a tablet and a bead can be mentioned suitably.

[0012] The approach of filling up an adsorption tower with an adsorbent and circulating this stock oil may be used for the contact to the stock oil and the adsorbent which were oxidized, and standing or the approach of stirring may be used for it in the stock oil oxidized by containers, such as a tank which fixed the adsorbent to the interior. The range of temperature of -40-100 degrees C is [the conditions in that case] desirable. - If there is a possibility that the fluidity of stock oil may fall if lower than 40 degrees C and it is higher than 100 degrees C, the adsorption capacity of an adsorbent falls and is not desirable. It is the range of -20-80 degrees C still more preferably. Moreover, as for a pressure, it is desirable that it is the range of ordinary pressure - 1 MPa-G.

[0013] Then, although stock oil is contacted to the 2nd devulcanizing agent, adsorption desulfurization of stock oil can be efficiently performed by using the 2nd devulcanizing agent. That is, it becomes extensible [temperature reduction of adsorption desulfurization of the 2nd devulcanizing agent or break time]. As this 2nd devulcanizing agent, there is especially no limit and it may use the adsorption devulcanizing agents or hydrodesulfurization catalysts other than the 1st devulcanizing agent. Especially a limit has that desirable from which there is nothing, the thing which is chosen from nickel, silver, chromium, manganese, iron, cobalt, copper, zinc, palladium, iridium, platinum, a ruthenium, a rhodium, and gold, and which contains a kind at least could be mentioned, and those metals were supported by porosity support especially as the adsorption devulcanizing agent. The aforementioned adsorbent can be mentioned as the porosity support. That with which the metal which contains nickel or silver at least especially was supported by porosity support is desirable. By carrying out hydrogen reduction beforehand, these

adsorption devulcanizing agents can raise the desulfurization engine performance. Moreover, when using a hydrodesulfurization catalyst as the 2nd devulcanizing agent, little addition of the hydrogen may be carried out. In addition, the temperature which uses the 2nd devulcanizing agent has desirable -40–300 degrees C. – If there is a possibility that the fluidity of stock oil may fall and it is higher than 300 degrees C when lower than 40 degrees C, the adsorption capacity of an adsorbent falls and is not desirable. It is the range of -20–250 degrees C still more preferably. Moreover, as for a pressure, it is desirable that it is the range of ordinary pressure – 1 MPa–G.

[0014] The method of contacting directly the stock oil desulfurized by the 1st devulcanizing agent to the 2nd devulcanizing agent as the desulfurization approach by the 2nd devulcanizing agent is desirable. Moreover, stock oil is desulfurized by the 1st devulcanizing agent in somewhere else, and the 2nd devulcanizing agent may be made to contact, just before carrying out a refining reaction. In the approach of this invention, as an organosulfur compound content liquefied oil, there is especially no limit and it can mention suitably natural gas, alcohol, the ether, LPG, naphtha, a gasoline, kerosene, gas oil, a fuel oil, an asphaltene oil, an oil sand oil, coal liquid, petroleum system heavy oil, Cher oil, GTL, a waste plastic oil, biotechnology fuel, etc. Kerosene is desirable especially and it is desirable that a sulfur content content especially applies to JIS No. 1 kerosene 80 ppm or less also in kerosene. This JIS No. 1 kerosene is obtained by desulfurizing the rough kerosene obtained by carrying out atmospheric distillation of the crude oil. If this kerosene remains as it is, it does not need to turn into JIS No. 1 kerosene, but it needs to reduce sulfur content. It is desirable to carry out desulfurization processing by the hydrotreating process currently generally enforced industrially as an approach of reducing this sulfur content.

[0015] The manufacture approach of the hydrogen for fuel cells which is the second invention of this application is an approach of manufacturing hydrogen, by doing in this way and contacting the stock oil which carried out desulfurization processing with a partial oxidation reforming catalyst, an autothermal reforming catalyst, or a steam-reforming catalyst (all being summarized and it only being hereafter, called a reforming catalyst). As a reforming catalyst used in the approach of this invention, there is especially no limit, out of the well-known thing known as a reforming catalyst of a hydrocarbon from the former, can choose the thing of arbitration suitably and can use it. As such a reforming catalyst, what supported noble metals, such as nickel, a zirconium or a ruthenium, a rhodium, and platinum, can be mentioned, for example to suitable support. A kind is sufficient as the above-mentioned support metal, and it may combine two or more sorts. In these catalysts, the thing (henceforth a nickel system catalyst) which made nickel support, and the thing (henceforth a ruthenium system catalyst) which made the ruthenium support are desirable, and the effectiveness which controls the carbon deposit in partial oxidation refining, autothermal refining, or steam reforming is large.

[0016] In the case of this nickel system catalyst, the amount of support of nickel has the desirable range of 3 – 60 mass % on support criteria. Under by 3 mass %, there is a possibility that the activity of partial oxidation refining, autothermal refining, or steam reforming may not fully be demonstrated, on the other hand, the improvement effectiveness of catalytic activity of having balanced that amount of support will seldom be accepted, but this amount of support will become disadvantageous economically rather, if 60 mass % is exceeded. When catalytic activity, profitability, etc. are taken into consideration, the more desirable amount of support of this nickel is five to 50 mass %, and its range of 10 – 30 mass % is especially desirable.

[0017] Moreover, in the case of a ruthenium system catalyst, the amount of support of a ruthenium has the desirable range of 0.05 – 20 mass % on support criteria. Under by 0.05 mass %, there is a possibility that the activity of partial oxidation refining, autothermal refining, or steam reforming may not fully be demonstrated, on the other hand, the improvement effectiveness of catalytic activity of having balanced that amount of support will seldom be accepted, but this amount of support will become disadvantageous economically rather, if 20 mass % is exceeded. When catalytic activity, profitability, etc. are taken into consideration, the more desirable amount of support of this ruthenium is 0.05 to 15 mass %, and its range of 0.1 – 2 mass % is especially desirable.

[0018] As a reaction condition in partial oxidation refining processing, as for 400–1,100 degrees

C, and oxygen (O₂)/carbon (mole ratio), 0.2 to 0.8 is adopted, and — for ordinary pressure — 5MPa and temperature, the conditions of 0.1–100hr⁻¹ are usually adopted for a pressure, as for liquid hourly space velocity (LHSV). moreover — as the reaction condition in autothermal refining processing — usually — a pressure — as for 0.1–1, and liquid hourly space velocity (LHSV), the conditions of 1,000–100,000hr⁻¹ are adopted [ordinary pressure — 5MPa and temperature / 400–1,100 degrees C, and steam/carbon (mole ratio)] for 0.1–10, and oxygen (O₂)/carbon (mole ratio), as for 0.1–2hr⁻¹ and the rate (GHSV) between gas space-time.

[0019] furthermore, a ratio with the carbon which originates in a steam and fuel oil as a reaction condition in steam-reforming processing — steam/carbon (mole ratio) — usually — 1.5–10 — desirable — 1.5–5 — it is more preferably selected in 2–4. If there is a possibility that the amount of generation of hydrogen may fall [steam/carbon (mole ratio)] less than by 1.5 and 10 is exceeded, a superfluous steam is needed and a heat loss is large, and since the effectiveness of hydrogen manufacture falls, it is not desirable.

[0020] Moreover, it is desirable to keep the inlet temperature of a steam-reforming catalyst bed at 630 degrees C or less and 600 more degrees C or less, and to perform steam reforming. If inlet temperature exceeds 630 degrees C, the pyrolysis of fuel oil may be promoted, carbon may deposit in a catalyst or a reaction tube wall via the generated radical, and operation may become difficult. In addition, although especially a limit does not have catalyst bed outlet temperature, the range of 650–800 degrees C is desirable. If there is fear which is not enough and it exceeds 800 degrees C, a reactor may need heat-resisting material and is not economically desirable.

[0021] reaction pressure — usually — ordinary pressure — 3 MPa-G — desirable — the range of ordinary pressure — 1 Ma-G — it is — moreover, LHSV — usually — 0.1–100hr⁻¹ — it is the range of 0.2–50hr⁻¹ preferably. In order that CO obtained by the above-mentioned partial oxidation refining, autothermal refining, or steam reforming may have an adverse effect on hydrogen generation in the manufacture approach of the above-mentioned hydrogen, it is CO₂ by the reaction about this. It is desirable to carry out and to remove CO. Thus, the hydrogen for fuel cells can be manufactured efficiently.

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EXAMPLE

[Example] Next, although an example explains this invention concretely, it is not restricted to these examples at all. The JIS No. 1 kerosene to be used is shown in the 1st table.

[0023]

[A table 1]

第1表

| 燃料油 | JIS1号灯油 |
|-----------|---------|
| 硫黄分 (ppm) | 48 |
| 蒸留性状 (°C) | |
| 初留温度 | 153 |
| 10%留出温度 | 176 |
| 30%留出温度 | 194 |
| 50%留出温度 | 209 |
| 70%留出温度 | 224 |
| 90%留出温度 | 249 |
| 终点 | 267 |

[0024] <Preparation of oxidation-treatment stock oil> oxidation kerosene 1 (oxidizer: meta-chloro perbenzoic acid)

5g (purity: about 70%) was added for the meta-chloro perbenzoic acid to 16l. of JIS No. 1 kerosene, it stirred at the room temperature for 8 hours, and oxidation kerosene 1 was obtained. Oxidation kerosene 2 (oxidizing agent: hydrogen-peroxide + salicylic acid)

13.6g was added for 4.5g (30% hydrogen peroxide) of hydrogen peroxide solution, and a salicylic acid to 16l. of JIS No. 1 kerosene, it stirred at the room temperature for 8 hours, and oxidation kerosene 2 was obtained.

[0025] [Example 1] 2l. of oxidation kerosene 1 was held in the container with a capacity of 5l., [Wakogel(trademark) C-200 and Wako Pure Chem industrial company make] made from silica gel 200g was added as an adsorbent, and it stirred at the room temperature for 24 hours. Then, filtration separated kerosene and an adsorbent. Subsequently, 15ml weighing capacity of the nickel support diatomaceous earth (nickel50 mass %, the whole nickel support diatomaceous earth criteria, nickel-5249, Engelhard Corp. make) was carried out as the 2nd devulcanizing agent, and the coil made from stainless steel with a bore of 17mm was filled up. After carrying out temperature up to 120 degrees C the bottom of ordinary pressure, and among the hydrogen air current and holding for 1 hour, temperature up was carried out further, it held at 380 degrees C for 1 hour, and nickel support diatomaceous earth was activated. Then, reaction temperature was lowered and held at 150 degrees C. To the coil, the collected aforementioned kerosene was circulated by liquid-space-velocity 10hr-1. The sulfur concentration of the kerosene after 5-hour progress was 0.13 ppm.

[0026] [Example 2] In the example 1, it carried out similarly except having used oxidation kerosene 2 instead of oxidation kerosene 1. The sulfur concentration of the kerosene after 5-hour progress was 0.15 ppm.

[Example 3] 2l. of oxidation kerosene 1 was held in the container with a capacity of 5l., [Wakogel (trademark) C-200 and Wako Pure Chem industrial company make] made from silica gel 200g was added as an adsorbent, and it stirred at the room temperature for 24 hours. Then, filtration separated kerosene and an adsorbent. Subsequently, 15ml weighing capacity of the silver support silica alumina (the whole Ag5 mass %;Ag support silica-alumina criteria, N-633L, the JGC chemistry company make) was carried out as the 2nd devulcanizing agent, and the coil made from stainless steel with a bore of 17mm was filled up. After carrying out temperature up to 170 degrees C the bottom of ordinary pressure, and among the nitrogen air current and holding for 3 hours, the temperature was lowered to the temperature fall. To the coil, the collected aforementioned kerosene was circulated by liquid-space-velocity 10hr⁻¹. The sulfur concentration of the kerosene after 5-hour progress was 0.15 ppm.

[0027] [Example 1 of a comparison] 2l. of oxidation kerosene 2 was held in the container with a capacity of 5l., [Wakogel(trademark) C-200 and Wako Pure Chem industrial company make] made from silica gel 200g was added as an adsorbent, and it stirred at the room temperature for 24 hours. Then, filtration separated kerosene and an adsorbent. The sulfur concentration of the kerosene was 6.9 ppm.

[0028] [Example 2 of a comparison] In the example 1, it carried out similarly except having used the JIS No. 1 kerosene which was not oxidized instead of oxidation kerosene 1. The sulfur concentration of the kerosene after 5-hour progress was 12 ppm.

[0029] [Example 4] (steam-reforming processing)

Steam-reforming processing was carried out with the refining vessel with which the lower stream of a river of the 2nd devulcanizing agent of an example 1 was filled up with 20ml (amount of ruthenium support 0.5 mass %, support criteria) of ruthenium system reforming catalysts. Refining processing conditions are a pressure:atmospheric pressure, the steam/carbon 2.5 (mole ratio), LHSV:1.0hr⁻¹, inlet temperature:500 degree C, and outlet temperature:750 degree C. Consequently, the invert ratio in the refining outlet of 200 hours after was 100%. Moreover, the sulfur content of the desulfurization processing kerosene in this reaction period was 0.2 ppm or less.

[Translation done.]